SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

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# CRFNEWS

COMBUSTION RESEARCH FACILITY

January/February 2005 • VOL. 27, NO. 1

## Coal-Burning Today is Significantly Cleaner, More Efficient Due to Decades of Research

*This article continues a series commemorating the CRF's 25th anniversary. Adel Sarofim, a former CRF Advisory Board member and longtime collaborator, highlights some of the CRF's significant contributions to coal utilization research. Sarofim is a Presidential Professor in the University of Utah's College of Engineering and Senior Technical Advisor to Reaction Engineering International.*

Coal is the nation's and world's largest fossil fuel resource and is responsible for over 50% of the United States' electricity generation. Its use in the U.S. has grown by 70 percent over the past 30 years even as power plant operators have had to meet increasingly strict air pollution standards.

Research conducted by the energy industry, academia, and government has led to a greater understanding of the science and technology of coal burning and 80-90%. reductions in $NO_x$ of new units since the 1960s. This is particularly significant as there is a resurgence in interest in coal-fired units with a projected addition of new capacity of 74 GW (~148 new plants) projected by 2025.

For many years, the CRF has brought its skills in laser and optical diagnostics and experience in the development of chemical kinetics models to bear on the complex processes accompanying coal utilization. This research has been supported by the Department of Energy's Office of Fossil Energy.

*(Continued on page 5)*

Sandia National Laboratories

*Clean Diesel*

# Dilute Clean Diesel Combustion Shows Promise for Meeting 2010 Emissions Regulations

New federal regulations further restricting heavy-duty diesel engine emissions that will go into effect in 2010 have prompted researchers to look for cost-effective in-cylinder strategies to curtail emissions without adversely affecting engine performance.

Building on previous work at the CRF, Sandia researchers Chuck Mueller and Ansis Upatnieks have taken a closer look at the potential of dilute clean diesel combustion (DCDC) for achieving lower emissions. Using diethylene glycol diethyl ether (DGE), a compound identified as a viable oxygenate for diesel fuel, they have found that DCDC shows considerable promise as a strategy for achieving 2010 emissions targets without the high cost of aftertreatment required with conventional diesel combustion, or the control problems of homogeneous charge compression ignition (HCCI)—another alternative.

Their research is sponsored by the Department of Energy Office of FreedomCAR and Vehicle Technologies and conducted in collaboration with heavy-duty and automotive diesel engine manufacturers.

### Spectrum of Approaches

The U.S. Environmental Protection Agency's 2010 regulations for heavy-duty diesel emissions—0.2 g/bhp-hr of $NO_x$ and 0.01 g/bhp-hr of particulate matter (PM)—represent reductions of more than 98% relative to 1988 standards (see Figure 1). Most of the research on in-cylinder emissions control is focused on using diluents to reduce in-cylinder temperatures, thereby limiting thermal $NO_x$ formation. The strategies range from those that use a premixed charge and volumetic reaction, such as HCCI, to those that use a stratified charge and mixing-controlled combustion, such as DCDC.

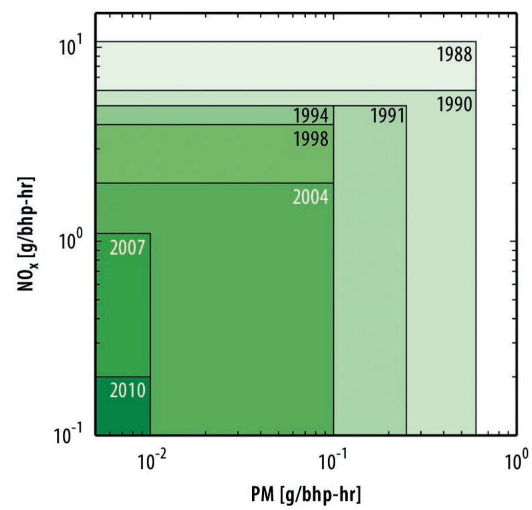



**Figure 1.** Tightening EPA emissions regulations for heavy-duty truck engines over time. Note logarithmic axes.

In DCDC, the dilute charge is produced by routing a fraction of the exhaust stream back to the intake manifold, a process known as exhaust-gas recirculation (EGR). One advantage of DCDC is that combustion phasing, and hence thermal efficiency, can be optimized simply by adjusting when the fuel is injected. However, the use of high EGR levels can lead to high PM emissions, long ignition delays, and unacceptably high pressure-rise rates as can sometimes occur under HCCI operation.

### CRF work on DCDC

Sandians Lyle Pickett and Dennis Siebers had explored the potential of DCDC to help achieve lower emissions through experiments in a constant-volume combustion vessel (see *CRF News*, November/December 2004). However, it was not clear whether the ignition delay and emissions of $NO_x$ and PM would remain small enough with high dilution to make the strategy practical for engine application.

*(Continued on page 6)*

# Sandia Microvalves Pave Way for New Health Care, Homeland Security Devices

Portable detectors for bioweapons and rapid screening tests for cardiac distress are just two of the potential applications for patented microvalves created in the Combustion & Physical Sciences Center.

Sandians Tim Shepodd and Dave Reichmuth are creating miniaturized fluid-handling components for novel microdevices for health care and homeland security applications. Just as electronic miniaturization has led to incredible increases in the power, speed, and portability of electronic equipment, reducing the volume of liquid-based devices enables rapid, sensitive, and portable chemical analysis.

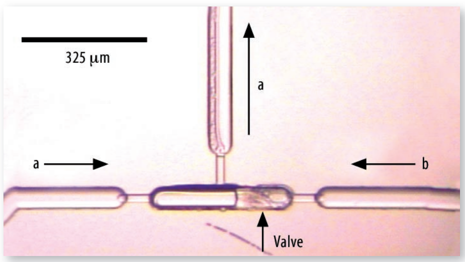



**Figure 1.** Example of an injector valve. The mobile polymer element slides in the center region, allowing the choice between solvents A and B. This valve can produce injections as small as 180 pl.

However, there are numerous challenges to adapt laboratory-scale processes to a microchip format. Components such as pumps and valves cannot be directly scaled down from benchtop to the microchip, so a need exists for novel methods to control very small volumes of fluid.

Sandia's microvalves allow high-pressure (up to 1000 psi) liquids to be routed inside a glass microchip. The valves are compatible with a range of commonly used analytical solvents, and can open and close extremely quickly (<10 ms). The microvalve concept was used to create an on-chip chromatography injector valve with picoliter sample size (see Figure 1). The analytical ability of the microchip was demonstrated by rapid separation of a protein mixture (see Figure 2). The valve's fabrication and performance is described in a recent *Analytical Chemistry* article (Reichmuth, D., et al., "On-Chip High-Pressure Picoliter Injector for Pressure-Driven Flow through Porous Media," *Anal. Chem.*, 76 (17), 5063–5068, 2004).

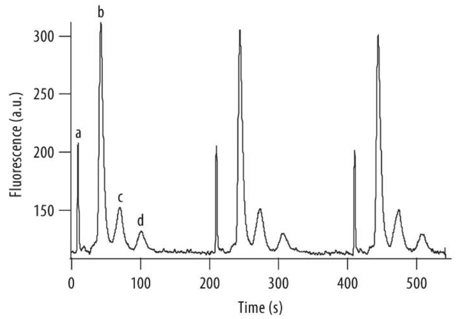



**Figure 2.** Repeated 640 pl, 750 ms injections of a protein mixture. Isocratic separation was performed using 24% acetonitrile + 0.16% heptafluorobutyric acid in 5 mM phosphate buffer (pH 2.0) at 300 psi. Peak identities: a. free dye b. insulin c. anti-biotin d. α-lactalbumin.

The valve can be used for different routing functions, such as an on/off valve, check valve, or micropipette (see Figure 3). In all cases, the valve is composed of a mobile polymer element that slides within a glass cylinder with constrictions that serve as valve seats. The glass structures are fabricated at Sandia using a multistep wet-etching process, and are later coated with a fluorinated, Teflon-like material to reduced friction between the glass and the valve element.

To form a polymer that matches the dimension of the channel exactly, an in situ polymerization process is used. A liquid monomer is placed into the channel. A narrow slit of light from a UV laser is projected onto the valve area of the channel, and photo-polymerization occurs. Once the unused polymer liquid is removed, a ~100 micrometer-long polymer element remains.

The microvalve is closed by sliding the polymer element against the valve seat (see Figure 3). The polymer slides in response to pressure differences between the inlet channels. Pressure pulses can be created in the fluid channels to quickly and easily control the valve element.

The mobile polymer microvalve concept originated with research on polymers for separations by Shepodd and former Sandians Jason Rehm and Charlie Hasselbrink. Early attempts at creating a microvalve were promising, but were not usable for chip-based fluid routing. Shepodd, Reichmuth, and former CRF researcher Brian Kirby developed new polymers and structures for microvalves that allow microchip separations. This most recent work received a 2003 R&D 100 award.

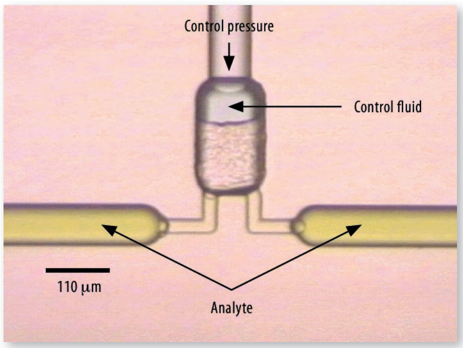



**Figure 3.** Example of an on/off microvalve. When the control pressure is higher than the analyte stream pressure, the valve moves downward and closes.

## Longtime CRF Director To Retire

Bill McLean, CRF Director for the past 12 years, will retire in early 2005. A new director is expected to be announced at that time.

McLean started his career at Sandia in 1978 in the Coal Combustion Division, working primarily on optical imaging of burning coal particles. He became supervisor of the Combustion Chemistry Division in 1981 and moved to the Combustion Technology Department as manager in 1984 before becoming CRF Director in 1992.

One of McLean's biggest accomplishments was the completion of CRF Phase II, which added 20,000-square-feet of laboratory space to the CRF and increased office space by 50%. It also provided new capabilities for users in chemistry, imaging, and diagnostics, and new facilities for sensor and engine research. Phase II has enhanced the CRF's leadership position in the international combustion R&D community by providing greatly enhanced capabilities for a broader set of users.

McLean also was instrumental in launching the microfluidics program, which started out about a decade ago as a spinoff technology from the CRF's chemical sciences and laser diagnostics expertise. It has been developed over the last decade into a handheld system called µChemLab™, a fully self-contained, portable chemical analysis system for detecting chemical and biological agents.

## Partnership to Develop Automated Water Safety Sensor Units

Sandia, CH2M Hill, and Tenix Investments Pty. Ltd. have formed a multiyear, multimillion dollar partnership to develop an unattended water safety system that offers the unique capability of detecting currently unmonitored biological agents such as bacteria, viruses, and protozoa that could threaten water supplies.

Current real-time, remote water quality monitoring is limited to detecting more traditional water-quality parameters, such as turbidity or the presence of dissolved solids, pH, nitrates, and ammonia.

The system will be based on microfluidics technology that arose from the CRF's chemical sciences and laser diagnostics expertise and has been developed over the last decade. The technology forms the basis for Sandia's µChemLab™ project, which centers on the development of a fully self-contained, portable, hand-held chemical analysis systems incorporating "lab on a chip" technologies.


CH2M Hill Senior Vice President and Chief Technology Officer Glen Daigger, Tenix Chief Operating Office Bob Leece, and Sandia Vice President Mim John.

## CRF Advisory Board

The CRF Advisory Board, pictured here with CRF management, conducted their annual review of CRF programs on Nov. 4 and 5. (Left to right) Bob Carling (CRF); Timothy Zwier (Purdue University), Ron Hanson (Stanford University), Brian Haynes (University of Sydney), Greg McRae (Massachusetts Institute of Technology), Bill McLean (CRF); Cathy Koshland (University of California, Berkeley), Jay Keller (CRF), Hukam Mongia (GE Aircraft Engines), and Andy McIlroy, Wen Hsu, Dennis Siebers, Don Hardesty, and Sarah Allendorf, all of the CRF. Not shown is board member Graham Hoare (Ford Motor Company).

### Fiber Laser Grand Challenge Launched; External Advisory Board Convenes at CRF

A research effort to advance the development of a high-powered fiber laser kicked off in December at the CRF with a meeting of the Fiber Laser Grand Challenge (FLGC) External Advisory Board. The board members attending represented the Defense Science Board, the Air Force Research Laboratory, the National Nuclear Security Administration Office of Nonproliferation Research and Engineering, and the Johns Hopkins Applied Physics Laboratory.

Funded internally through the Laboratory Directed Research and Development program, the goal of the FLGC is to develop a new laser technology to enable miniature, ultra-efficient, high-power devices that will revolutionize the application of lasers to real-world problems. The program is based on a patented Sandia technology for power scaling of rare-earth-doped lasers using a fiber coiling technique (see *CRF News*, July/August 2002 and March/April 2001).

The board is tasked with providing an objective review of the program's goals and technical approach, fresh ideas on research directions, and bridges to future funding. Dahv Kliner is the project leader and Wen Hsu is the program manager.

Postdoc Mike Leavell has taken a position as a postgraduate researcher at the new Genome Center at the University of California, Davis. For the past two years, Leavell had been part of a team led by Rich Behrens working on biological mass spectrometry.

# Adams, Bastress Award Recipients Announced

(Left to right) Engine Combustion Manager Dennis Siebers, award recipients Stephen Klippenstein and Paul Miles, and CRF Director Bill McLean.

Stephen Klippenstein and Paul Miles are the most recent recipients of the Adams and Bastress Awards, respectively—awards established nearly 20 years ago in memory of two key individuals in the CRF's history.

Bill Adams was the CRF's original, highly supportive sponsor from the U.S. Department of Energy. Klippenstein received the award for extraordinary contributions in computational chemical kinetics and combustion chemistry that enable substantial insights in areas ranging from elementary chemical dynamics through fundamental chemical kinetics to combustion modeling.

Karl Bastress guided the DOE's initial energy conservation-related combustion research activities and encouraged applied and interdisciplinary research linking the fundamental understanding of combustion processes to the practical development of combustion technology. Miles received the award for developing a new and comprehensive understanding of in-cylinder fluid mechanic processes in direct-injection, automotive diesel engines that has transformed the understanding of turbulence generation and its impact on fuel-air mixing and combustion in these engines, and for excellence in transferring this knowledge to diesel engine developers.

# CRF Assists State Air Resources Board

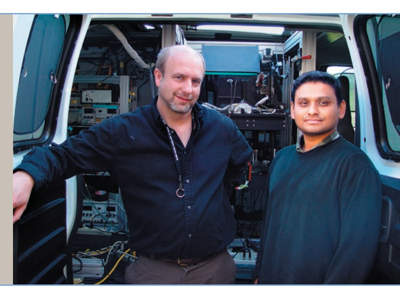
Sandia technologist Lloyd Claytor assists with the LII demonstration at CARB's Stockton test facility.

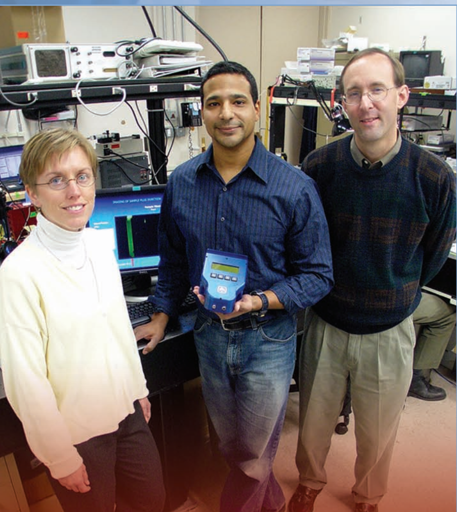
At the request of the the California Air Resources Board (CARB), CRF engineer Pete Witze recently conducted a week-long field demonstration of his laser-induced incandescence (LII) system at the agency's heavy-duty chassis dynamometer test facility in Stockton, Calif. The demonstration was designed to familiarize CARB with the LII technique, and show first-hand that it has the capability to measure particulate matter (PM) emissions on-board a heavy-duty diesel truck in operation.

This capability will be essential in achieving compliance with more stringent federal emissions regulations—called "not-to-exceed" (NTE) limits—that take effect in 2007. California regulators have scheduled a pilot NTE study to begin in 2005.

A task force comprising the U.S. Environmental Protection Agency, the Engine Manufacturers Association, and CARB is evaluating portable emissions measurement systems (PEMS) to be used by the heavy-duty diesel engine manufacturers. Conventional, filter-paper PM measurement techniques that have been used in the past are inadequate for taking transient, on-road measurements. LII has demonstrated the ability to measure "real-world" particulate emissions in a vehicle under actual driving conditions (see *CRF News*, March/April 2004).

Postdoc Sanjay Devdas (right) left the CRF in November to return to India. For about the past three years, he had been working with Tom Kulp and Tom Reichardt (not pictured) on a natural gas mapper for the Gas Technology Institute.





Former postdoc José Cintron (center) begins employment at Eli Lilly and Company in February. Cintron had worked for two years on the µChemLab project under the direction of Sandians Julie Fruetel and Mark Allendorf.

## Two Sandia Research Groups in Top 10 for Laboratory Automation Innovation Award

The work of two Sandia research groups is among the top 10 contenders for the Association for Laboratory Automation (ALA) Innovation Award, having been chosen from a pool of 120 oral presentations. The $10,000 award recognizes the presentation at the LabAutomation conference that best contributes to the exploration of technologies in the laboratory, and comprises independence of thought, clarity of vision, extraordinary technical originality, and seminal integration andautomation strategies.

**In the top 10 are:**

- Amy Herr, and coauthors Dan Throckmorton and Anup Singh, for work on innovative on-chip electrokinetic immunoassays for rapid, sensitive quantitation of proteins associated with human immune system response.

- Yolanda Fintschenko, and coauthors Eric Cummings, Blake Simmons, Greg McGraw, Rafael Davalos, and Blanca Lapizco-Encinas, for work on the insulator-based dielectrophoresis (iDEP) concentrator, a new approach for detecting pathogens in water that reduces the sample volume needed to successfully deliver a detectable amount of pathogenic material to an analytical device.

The award recipient will be announced Feb. 4 at the LabAutomation conference in San José, Calif.

The ALA is a nonprofit association with a membership of more than 1300 scientists supporting the advancement of automation technologies worldwide.

# Coal-Burning *(Continued from page 1)*

### Challenges of boiler modifications

Coal in the U.S. is used primarily in pulverized coal-fired boilers, many of which have been in service for over 40 years. Modifications to these boilers to meet emissions standards have often led to problems with flame stability, unburned carbon in the fly ash leaving the boiler, and changes in heat transfer to the boiler surfaces because of ash deposition.

To help address these problems, the CRF established three specialized facilities with optical access to allow in situ observations of single particles, providing fundamental data in the following areas:

- The release of volatiles by coal, important for stabilizing the flames;
- The kinetics of char (the solid residue after volatile release) burnout, important for achieving high combustion efficiency;
- The transformation and deposition of ash particles formed by inorganic constituents in coal that impact heat transfer to boiler surfaces.

The application of difficult and unique laser and optical diagnostic techniques in these facilities has yielded major new insights into these complex processes and spurred the development of predictive computer codes.

### Understanding devolatilization

Devolatilization—the rapid release of gases during the heating process in a combustion chamber—has a significant effect on flame stability in pulverized coal fired boilers. The CRF developed new methods to characterize the molecular structures of the parent coals and the char and tars produced during devolatilization, information that was used to develop detailed chemical models. Early on, CRF researchers obtained the first direct images of volatile compounds forming soot in the wakes of burning individual pulverized coal particles, with later studies showing that the soot is formed from the tars in the volatiles.

Using solid state nuclear magnetic resonance (NMR), researchers at the CRF in collaboration with colleagues at the University of Utah quantitatively characterized the structure of coals, and the volatile and char products yielded upon heating. The coal structure was described as a network of interconnected fused ring aromatic structures with side chain constituents. A chemical percolation devolatilization (CPD) model was developed to show how the volatiles are released by the breakage of the bridges connecting the aromatic groupings to each other and to side chains containing carboxy, hydroxyl, nitrogen, and sulfur entities. These breakages determine the rate of release and composition of volatiles. The residual char is produced by competing crosslinking reactions between the aromatic groupings.

Parallel experimental studies were conducted to refine the models on the rate of volatiles release, made possible by the development of an infrared optical pyrometer which eliminated biases introduced by radiation reflected from furnace walls. The capability for accurate particle temperature measurement contributed to a reduction of uncertainties of up to five orders of magnitude in the rates of high-temperature devolatilization previously reported in the literature.

### Role and behavior of chars

The CRF has also contributed greatly to the understanding of char burnout kinetics, an important factor governing efficiency. CRF researchers measured the oxidation rate of a wide range of chars in a laminar flow reactor that provided optical access for study of the trajectories, sizes, shapes, and temperature of individual particles. The combination of the unusually precise measurements and the sophistication of the models developed to interpret the data provided unparalleled details on particle-to-particle variations in burning rate, density, emissivity, and diameter. The reaction rates, obtained from the differentials between the particle and gas temperatures, were summarized in a Sandia Milestone Report[†] that has become an international resource.

The studies at Sandia produced unique information showing that the reactivity of chars decayed significantly during the last stages of burnout, which explains the amount of unreacted char in the fly ash collected from full-scale boilers. The reaction rate measurements were complemented by studies of the fine structure of char particles extracted from the reactor and detailed high-resolution video studies of single particles held in place in the reactor. High-resolution electron microscopic examination indicated that part of the decay in char reactivity at high burnouts was due to low-reactivity turbostratic microstructures (with graphite-like layering) formed by the carbon. The captive particle study indicated that high coverage of the char particle surface by fly ash also contributed to the decay in reactivity. The results provide the foundations for the char burnout kinetics (CBK) model now widely used internationally in computational fluid dynamics codes of coal-fired boilers.

### Ash and boiler efficiency

Fly ash deposition in boilers has an adverse effect on heat transfer and therefore boiler efficiency. The formation of an insulating ash layer on tube surfaces alters their ability to absorb radiation or transfer heat by conduction. Plant operation is maintained by the use of steam jets (so-called soot blowers) to periodically blow off such deposits.

The CRF developed a comprehensive program for studying fly ash deposition on heat transfer surfaces, using in situ optical probes to follow the trajectories of particles onto a tube surface. These were accompanied by complementary spectroscopic studies to study concomitant variations in surface absorption of radiation at different wavelengths as a function of coal type, including mixtures of coal cofired with biomass. Models were developed for the insulating properties of the very porous ash layers produced, allowing for optimization of strategies for the placement and operation of soot blowers.

### Coal's future

With a 250-year reserve/production ratio of this domestic, low-cost fuel, the U.S. is likely to continue using coal as a major component of its energy portfolio for the foreseeable future. But conventional power plants increasingly will be replaced with integrated gasification combined cycles (IGCC) or oxy-fueled (burning a fuel, such as coal, in oxygen rather than air) plants to meet anticipated requirements for carbon management. The CRF is well positioned to provide the basic data needed to design these plants with their recent research on oxy-coal combustion and construction of a reactor that can provide char gasification kinetics at the high pressures utilized in IGCC plants.

[†] R.E. Mitchell, R.H. Hurt, L.L. Baxter, D.R. Hardesty, "Compil. of Sandia Coal Char Comb. Data and Kinetic Analyses: Milestone Report," Sandia Tech. Report (1992).

# Clean Diesel

(Continued from page 1)

Mueller and Upatnieks have been studying DCDC using a single-cylinder optically accessible engine in the CRF's Advanced Fuels Laboratory to determine whether it can help meet the 2010 heavy-duty engine regulations. They selected neat DGE for the work because it is highly oxygenated and was therefore expected to lower PM emissions, and because it has a very short ignition delay, which was expected to help maintain pressure-rise rates within acceptable levels.

Figure 2 shows results from the experiments—run at steady-state conditions—plotted as a function of the mole fraction of oxygen in the intake charge. $NO_x$ emissions are below the 2010 limit when the oxygen concentration is less than approximately 14%, and smoke emissions are believed to be near or below the 2010 limit over the range of oxygen concentrations in the study. Efficiency does not begin to decline until the oxygen concentration drops below approximately 11%.

The Figure 2 inset shows that heat-release rates are even lower under DCDC than for traditional diesel combustion, which should lead to quieter engine operation. Natural luminosity images of the in-cylinder combustion process show relatively minor changes to the reacting jet structure (e.g., flame lift-off length, diffusion flame shape) with increased dilution. However, the total natural luminosity signal intensity drops by two orders of magnitude as the oxygen concentration is lowered from 21% to 10%, indicating significant decreases in soot volume fraction and/or temperature under DCDC operation.

Results similar to those shown in Figure 2 have been acquired at up to 18 bar gross indicated mean effective pressure (IMEP), which represents 3/4-load operation. Future work will continue to explore fuel effects on DCDC using both traditional and optical diagnostics.

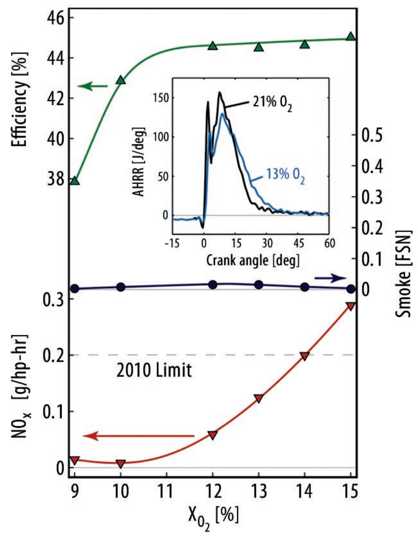



**Figure 2.** Engine-out $NO_x$ and smoke emissions, fuel-conversion efficiency, and apparent heat-release rate (AHRR, inset) data acquired under DCDC conditions. 2010 emissions targets can be achieved without a significant efficiency penalty for steady-state operation with an oxygen mole fraction between approximately 11% and 14%, using DGE fuel, at an engine load of 7.0 bar gross IMEP. The 1.7 liter single-cylinder engine has a compression ratio of 11.3:1 and was operated at 1200 rpm with an intake temperature and pressure of 25°C and 2.23 bar (absolute), respectively. EGR was simulated with nitrogen gas.

## Behrens, Maharrey Receive Best Paper Award from Chemical Propulsion Group

Rich Behrens and Sean Maharrey have received a best paper award from the Joint Army, Navy, NASA, Air Force (JANNAF) Combustion Subcommittee/Propulsion Systems Hazards Subcommittee. The paper, "Reaction Kinetics of RDX in the Condensed Phase," describes the development of a mathematical model of the reaction processes that control the thermal decomposition of RDX in the liquid phase. JANNAF is an organization focused on technical work related to chemical propulsion.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CRF News is a bimonthly publication of the Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551 0969.
ISSN 1548-4300

Director ........ William J. McLean
Editor ........ Julie Hall
Graphic Artist ........ Daniel Strong
Photography ........ Daniel Strong & various photographers

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*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC0494AL85000*